INVESTIGATION ON EFFECTS OF ROASTING TEMPERATURE AND ROASTING TIME ON CAFFEINE CONTENT IN COFFEE USING OPTICAL METHOD

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Abstract

In this work a simultaneous determination of caffeine content was performed in sample of sidamo (Ethiopia) coffee, before and after roasting at either different temperature $(140 - 210^0 c)$ and different exposure time $(4 - 10\,\mathrm{min})$ in order to investigate the effect on roasting temperature and roasting time on the content of caffeine content in coffee. A UV/VIS spectrophotometer method was used. A modest losses of caffeine was verified both in the roasting time and roasting temperature. Rate constant for chemical reactions at $200^0 c$ were determined. The result shows weight loss increases during roasting. For a pure caffeine molar decadic absorption coefficient and translational dipole moment were $(1054 m^2/mol)$ and $(12.78 \pm 0.71)\, cm$ respectively.

Key words: coffee, caffeine, roasting, uv/vis spectrophotometer, thermal.

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Contents

Chapter 1
Introduction

Coffee is one of the most valuable primary products in world trade,in many years second in value only to oil, as a source of foreign exchange to developing countries [1] .

Coffee belongs to the family Rubiaceae and to the genus coffea [2] .Rubiaceae has over 6000 species and 500 genera.Of these, the most economically important genus is coffea [3],comprising about 100 species [4] .The species of the genus coffea are indigenous to Africa, Madagascar and the Mascarenes.

All species of coffea are woody, ranging from small shrubs to large robust trees with heights up to 10m. Phenotypic variation between species is enormous. Some are deciduous while others are evergreen. Leaves range in color from yellow and dark-green to bronze and purple-green; their size vary from 1 to 40cm in length, coffea Liberica L. having the largest leaves. Species differ considerably in the type of fruit they bear, ranging from being good and sweet flavoured to being distinctly inedible.Fruit size ranges from that of a small pea to a good-sized plum. Flowers range from being small, unattractive and scentless to being large and densely clustered with abundant fragrance. Some species have white flowers, some pink or almost purplish and some creamy to yellowish [3] .

The genus coffea is diverse and reported to comprise about 100 species [4], only two species namely (coffea Arabic) and robusta (coffea canephora) are under

commercial cultivation.Arabica, the highland coffee, accounts for 60-70% of coffee is more adaptable to lowlands and contributes the remaining 30-40%. Arabica coffee produces superior quality coffee but its yield is very low, often constrained by diseases and pests [5] .

Arabica coffee is the only known tetraploid(2n=4x=44) and self-fertile (over 95%) species in the genus [6]. It is the most widely cultivated and one of the oldest known species.Arabica coffee is monocentric since its center of origin and diversity is Ethiopia [7].

Coffee has been used by Ethiopians before its migration to Arabia Felix(Yemen).However, the history of coffee as economically important crop goes back only to the 15^{th} century when the world supply came from Yemen [8] currently, it is the world′S most popular non-alcoholic beverage is exported in various forms to more than 165 countries and generates on average us $9.7 billion annually [2].

Coffee production through out Ethiopia can be put in to two categories based on its level of production as major and minor coffee growing regions.

IIlubabor, Wellega, Keffa, Sidamo, Gedeo and Harrage are the major coffee growing regions in Ethiopia, since their coffee contribution is 95% of the total coffee production in Ethiopia. Arssi, Shoa, Gojjam, Gonder and Wollo are where coffee is not produced as major production but, it only satisfies the local consumption. This region of the country is considered minor coffee growing region.

Coffee is a very important crop for the least developed countries in Africa. For some of them it is vital. In countries like Ethiopia, Burundi, Central Africa, Republic of Tanzania, coffee is one of the main export product. The performance of the coffee sector in these countries affects the overall performance of their export and their economic growth [9] .

In Ethiopia, coffee contributes over 5% of the gross domestic product, 12% of the agricultural output, 70% of the foreign exchange earning and 10% of the government revenues. Besides, 25% of the population is employed in coffee production, processing and marketing [10] . About 400,000ha land is covered by coffee and the annual national coffee production is estimated to be 200,000–250,000 ton [11] .Of this, 80% is dry processed (natural) coffee and about 35% is consumed locally. Ethiopia ranks first in coffee consumption in Africa and the annual national average per capita coffee consumption is 3kg. Small-scale coffee farms contribute about 90% while large scale modern plantations account for the remaining 10% coffee production of the country.

Many social aspects of coffee can be seen in the modern-day life style. The united states is the largest market for coffee, followed by Germany and Japan [1] . The Nordic countries consume the most coffee per capita, with Finland typically occupying the top spot with a per-capita consumption in excess of 10kg per year consumption has also vastly increased in the United Kingdom in recent years, but as of 2005, was still below 5kg per year.

The history of introduction of arabica coffee from Ethiopia to Yemen is still vague [12] reported that the first migration of arabica coffee from Ethiopia to Yemen was during the period of prehistoric trade. It was [3] suggested that arabica coffee plants could have been introduced to Yemen as early as 575AD and again by about 890AD by Persian armies from Harar, Ethiopia. On the other hand, [13] it is reported that c.arabica was introduced to Yemen three to four centuries ago. Similarly, [14] it is reported that Arabs introduced coffee from Ethiopia to Yemen during the fifteenth century.

Historical data indicated that the introduction of arabica coffee to other countries first occurred from Yemen to the Malabar coast of India by Baba Budan in 1600 and from there to Ceylon and Java in the last decade of the 17^{th} century. From Java a single coffee plant was taken to the botanical garden of Amsterdam in 1706 [14] . It was from this tree that c.arabica was propagated and spread to Asia, South America, parts of Africa and some botanical gardens in Europe. The other c.arabica sources were those collected by French men from Mocha (Yemen) in 1715 and 1718 and planted on Reunion (Bourbon) Island and from this source the Bourbon coffee of the world was propagated. Therefore, the spread of arabica coffee around the world was based on a very limited number of trees. The seven berries taken by Baba Budan to India, the small shipment to Reunion and the tree taken from Java to Amsterdam in 1706 together with its progeny in Paris.

There are four main coffee production systems in Ethiopia, namely forest, semi-forest, garden and plantations forest and semi-forest coffee production systems account 33% of the land covered by coffee and 25% of the annual coffee production in the country.On the other hand the remaining two systems represent 67 and 75% of area and production of coffee of the country, respectively. The contribution of forest coffee production system is dwindling as a result of deforestation [15]. However, the forest coffee production system is still serving as a reservoir for arabica coffee genetic resource.

Coffee′S bioactive profile contains many of the most important constituents known to exit within functional foods: flavonoids(catechins, anthcyanins); caffeic acid, and ferrulic acid. Additional biologically active components found in coffee include nicotinic acid, pyrogallic acid and caffeine [16] .

Coffee is a rich source of antioxidants, including those derived from the hydroxycinnamic acids, family(caffeic,chlorogenic, coumaric, ferulic and sinapic acids), flavonoids,and polyphenols.

The water soluble constituents of coffee are: phenolic polymers(pulp) 8%, polysaccharides 6%, chlorogenic acids 4%, minerals 3% ,water 2%, caffeine 1%, organic acids 0.5%, sugars 0.3%, lipids 0.2%, and aroma 0.1% [17].

Roasting is a time-temperature dependent process, whereby chemical changes are introduced in the green coffee, with a loss of dry mass primarily as gaseous carbon dioxide and other volatile products of the pyrolysis. About half of the total carbon

dioxide generated will be retained within the roasted coffee, together with a major proportion of the important volatile flavour substances.

Roasting is normally carried out under atmospheric pressure with hot air and combustion gases as the primary heating agent, though heat may also be provided by contact with hot metal surfaces, solely or supplementary. After the initial removal of moisture,roasting proper starts at a green bean temperature of about 200^0c after which through exothermic reactions, escalation of effect readily occurs requiring considerable control of the process for a given degree of roast.

Chemical composition, of both volatile and involatile substances will be strongly determined by the degree of roasting.

In roasting, times of heating range in practice from a few minutes to about 30 minutes; beyond that time is generally regarded as undesirable for the flavour. For any given degree of roast, the time is determined by conventional heat transfer factors, i.e. the relative movement of the beans-air(velocities), bean-bean and bean-contact surfaces together with any internal radiative heat effects.

The physical changes in the coffee beans during roasting are also technically important. Expansion of the beans takes place, including a ′popping′ phase, leading to considerably decreased density, as function of degree of roast but also of the speed of roasting. This decrease of density is followed through in to the ground roasted coffee, as a decrease of bulk density.

At the start of the roasting process loosely bound water is drive off and some shrinkage occurs particularly with arabicas. As evaporative cooling declines, so the bean temperature rises and an exothermic pyrolysis begins in the temperature range 140^0c-160^0c, and leads to the formation of the well-known color, aroma and taste of roasted coffee products. The pyrolysis peaks between 190^0c and 210^0c with enthalpies of 230 to 375J/g, and charring begins at about 230^0c if it is not arrested.

Excessive temperature during roasting is known to cause undesirable chemical changes, especially at the bean surface requiring considerable control of the process and objective means for its quality control [18] .

During the roasting of green coffee the bean temperature will be raised, by a combination of external heating and exothermic chemical reactions to above 200^0c. It is found in practice that the losses are relatively modest and, unless severe roasting conditions are employed , rarely amounts to more than a few percent. As the weight of the green beans will be reduced by up to 20% or more (say 10% water, 10% dry matter) during roasting, the actual percentage amount of caffeine may increase by up to 10% on a dry roasted basis. The reasons for this modest loss of caffeine are complex, but the two major contributing factors are probably an increase in the sublimation point of caffeine as a result of pressure build up within the bean and a poor rate of diffusion of vapor through its outer layers. Caffeine will also form salts as a result of the mildly acidic conditions which increase during roasting, but as these

salts are relatively weak they will decompose and thus should have little effect on the sublimation process [19] .

Caffeine is a naturally occurring substance found in the leaves, seeds or fruits of over 63 plants species worldwide and is part of a group of compounds known as methylxanthines.The most commonly known sources of caffeine are coffee, cocoa beans, cola nuts and tea leaves. Caffeine is a pharmacologically active substance and depending on the dose, can be a mild central nervous system stimulant. Caffeine does not accumulate in the body over the course of time and is normally excreted within several hours of consumption [20] .

Caffeine is an alkaloid of the methylxanthine families its pure state, it is an intensely bitter white powder. Its chemical formula is $C_8H_{10}N_4O_2$,its systematic name is 1,3 5-trimethylxanthene.

Pure caffeine occurs as odorless,white fleccy masses, glistening needles of powder. Its molecular weight is 194.19g, melting point is 236^0c, point at which caffeine sublimes is 178^0c at atmospheric pressure, pH is 6.9(1% solution), specific gravity is 1.2, volatility is 0.5%, vapor pressure is 760mmHg at 178^0c, solubility in water is 2.17%, vapor density 6.7 [21] .

The world'S primary source of caffeine is the coffee bean (the seed of the coffee plant), from which coffee is brewed. Caffeine content in coffee varies widely depending on the type of coffee bean, the method of preparation used, even beans within a given bush can show variations in concentration [22] .

Caffeine has a high temperature coefficient of solubility in water. This property is advantageously used to crystallize out pure caffeine. The solubilities are 2.2% caffeine at room temperature, 15% caffeine at 80^0c, and 40% caffeine at100^0c [23] .

Caffeine and its major metabolite, theophylline, are widely distributed in plant products. Similar to other methylxanthine derivatives, they can cause various physiological effects such as relaxation of bronchial muscle, stimulation of the central nervous system, gastric acid secretion and diuresis [24] .

Caffeine intake and coffee consumption increase our experience of stress by stimulating the release of the stress hormones cortisol, epinephrine, norepinephrine and the gluconticoids. The continuous presence of these hormones not only has damaging effect on a number of different physiological systems, but can also accelerate the aging process.Although short-term stress can be physiologically motivating and can mobilize physiological processes, the extended presence of stress- related hormones is detrimental and damaging [25] .

Caffeine is a central nervous system and metabolic stimulant, and is used both recreational and medically to reduce physical fatigue and restore mental alertness when unusual weakness or drowsiness occurs. Caffeine stimulates the central nervous system first at the higher levels, resulting in increasing alertness and wakefulness, faster and clear flow of thought, increased focus, and better general body coordination, and later at the spinal cord level at higher doses [26] .

Acute caffeine intake has been shown to significantly increase central blood pressure as well as systolic and diastolic blood pressure while people are drinking coffee at work. Drinking coffee within three hours causes a measurable rise in both systolic and diastolic blood pressure, and that effect can persist even in to the following day. In people prone to hypertension, drinking coffee may be harmful. Decaffeinated coffee also increase blood pressure, stimulates heart rate and increases sympathetic nervous system activity in muscle tissue.

Coffee and caffeine interfere with absorption and increase extraction of several vital minerals necessary for maintaining cardiovascular health, preventing bone density and preventing chronic diseases, including calcium, potassium, magnesium and iron. In the U.S. today, 10 million people are diagnosed with asteoporosis and 34 million more suffer from low bone mass, which subsequently increases their risk of developing osteoporosis or associated fractures. With increasing age, the probability of developing osteoporosis also increases.

Coffee and caffeine also decrease levels of the steroid hormone, dehydroepiandrosterone, commonly known as DHEA. DHEA seems to have a protective effect on the body and appears to be involved in defending against the negative effects of aging. Some of the physical and physiological changes of aging are related to the decline of many hormones including DHEA that assist in repair of cells and tissues, enhance cognition and memory, and help maintain the body physiological processes [27] . Caffeine and coffee negatively impact these complex hormonal systems.

Caffeine is moderately soluble in a wide range of organic solvents even at relatively low temperatures. Of these solvents many have been used for decaffeination, although in recent years dichloromathane(methylene chloride) is the most widely used. It is also soluble in supercritical carbon dioxide and this solvent has been more recently used for decaffeination on account of possible toxic effects of methylene chloride residues.

Caffeine absorbs strongly in the ultraviolet region ($\lambda_{\max}$ 272 nm in water and 276 nm in chloroform) and this provides the basis of innumerable spectrophotometric methods [19] .

Commercial decaffeination of coffee was commenced in Germany early in the twentieth century and a little later in the USA. Although for many years sales were fairly static, consumption of decaffeinated coffee has more recently shown an increase, some 10% of world production of green coffee now being treated in this way. In some European countries as much as 20% of coffee imports may go for decaffeination, although in the UK the proportion treated is relatively insignificant.

The original process for removing caffeine involves wetting the green bean with superheated steam and extracting them with a solvent, originally chloroform or benzene, later trichloroethylene, and more recently dichloromethane(methylene chloride). The solvent is then removed by steam distillation and the beans dried to near their original moisture content. An alternative method, avoiding contact with chlorinated solvents, is known as water extraction, and is carried out in a battery

of percolators. Many patterns exist for other methods of decaffeination; the use of aqueous liquid carbon dioxide as a solvent is frequently mentioned.

After decaffeination, the green beans have usually lost their greenish, color, and in earlier days the subsequently roasted coffee a great deal of its flavour, although this defect has since been largely overcome by improved technology.

Most countries impose a limit on the residual caffeine content for a coffee to be described as decaffeinated; in the EEC countries, roasted coffee and soluble coffee must not contain, respectively, more than 0.1% and 0.3% of the dry matter content as caffeinection, etc.)

For caffeine content determination from roasted coffee many analytical methods have been reported. Normally,high-performance liquid chromatography separation and uv/vis spectrophotometer detection methods are applied. Also other methods such as capillary electrophoresis,thin layer chromatography and gas chromatography,are used for separation of caffeine in the analysis of mixtures,combined with several other detection methods such as mass spectroscopy and FTIR spectrophotometric measurments. However, very costly instrumentation,highly skilled tecnhnitials and complicated and time consuming procedures are required for such methods [28] .

Spectrophotometer method is simple sensitive, rapid, reproducible valid and the most suitable for on line monitoring,when considerable attention is paid to the removal of interfering compounds using mathematical methods.

Thus, the purpose of this study is investigation on effects of roasting temperature and roasting time on caffeine content in coffee using Uv/vis spectrophotometer. The effects and consequence of temperature on caffeine will be investigated using TGA.

Chapter 2
Spectroscopy

2.1 Introduction

Spectroscopy is the study of the interaction of light and matter, a study that encompasses a wide range of physical and chemical behavior. Spectroscopy plays an important role in the emergence and validation of quantum theory in the early twentieth century. Max plank′s analysis of the emission spectrum of a blackbody radiation established the value of his eponymous constant, setting in motion a revolution that drastically altered our picture of the microscopic world.

Modern quantum theory smeared the sharp orbits of Bohr′s hydrogen atom into probability distributions, and successfully reproduced the observed spectral transition frequencies. Observations of electron emission by irradiated metals led to Einstein′s theory of photons as packets of light energy, after many hundreds of years of debate on the wave-particle nature of light. Experiments(such as electron diffraction by crystals) and theory(the Schrodinger equation and the Heisenberg uncertainty principle) gave rise to the idea that matter, like light, has wave-like as well as particle-like properties. Quantum theory and Einstein′s concept of photons converge in our modern microscopic view of spectroscopy.

A typical spectrum consists of the intensity of a certain response, such as absorption of light, as a function of frequency of the light. The intensity is a measure of the rate at which molecules make transitions from one energy level to another, while the frequency is directly related to the difference in the initial and final energies of the molecule [29] .

Several processes leading to emission or absorption may occur in the atom or molecule, to a good approximation each of these processes is associated with radiation of very different frequency ranges. Several types of spectroscopy may be distinguished on the bases of the frequency range in which measurements are made as well as the type of information sought [30] .

Molecular spectroscopy is the study of the absorption or emission of electromagnetic raditaion by molecules. The experimental data that such studies provide are the frequencies, or wavelengths, of the radiation and the amount of radiation emitted or absorbed by the sample.

One can often understand the nature of the molecular charges that are responsible for the emission or absorption of the radiation. In such cases, the experimental spectroscopic data can be used to determine quantitative value for various molecular properties.

When the theory of molecular spectra is treated, it is convenient to classify spectra according to the type of molecular energy that is being altered in the emission

and absorption process. In this way the principal headings for the material that is to be presented can be arrived at. These are:

Rotational spectra–due to changes in the rotational energy of the molecule.

Vibrational spectra–due to changes in the vibrational energy of the molecule.

Electronic spectra–due to changes in the energy of the molecule due to different electron arrangements.

The quantized internal energy E_{int} of a molecule in its electronic ground or excited state can be approximated with sufficient accuracy for analytical purposes, by

$$E_{int} = E_{el} + E_{vib} + E_{rot} \tag{2.1}$$

where E_{el} is the electronic, E_{vib} the vibrational and E_{rot} the rotational energy respectively. Absorption of a photon results in a change of the electronic energy accompanied by changes in the vibrational and rotational energies. Each vibronic transition, i.e. a particular electronic plus vibrational transition, corresponds to an absorption band consisting of the rotational lines In liquids and solids the rotational lines are broad and overlap so that no rotational structure is distinguishable.

2.2 Effect of an Electromagnetic Field on Charged Particles

The classical expression for the force experienced by a charged particle in an electromagnetic field is known as the Lorentz law:

$$\overrightarrow{F} = q\left(\overrightarrow{E} + \overrightarrow{v} \times \overrightarrow{B}\right) \tag{2.2}$$

where q is the charge and $\overrightarrow{v}$ its velocity. Classical mechanics provides us with prescriptions for expressing the momenta of particles in terms of the classical Hamiltonian or Langrangian, both of which are functions of the kinetic energy T and potential energy V of the particle. In the absence of a field, the classical Hamiltonian for a single particle is given by

$$H = T + V = \frac{p^2}{2m} + V \tag{2.3}$$

where p is the momentum,m is the mass, and the potential energy V is a function of the position. The substitution $\overrightarrow{p} \longrightarrow \overrightarrow{p} - e\overrightarrow{A}$ results in a Hamiltonian that is consistent with the force given by $Eq.\,(2.2)$ .So in the presence of an electromagnetic field, the Hamiltonian should be written as

$$H = \frac{1}{2m}\left(\overrightarrow{p} - e\overrightarrow{A}\right)^2 + V \tag{2.4}$$

The classical Hamiltonian is converted to a quantum mechanical operator simply by replacing the momentum $\overrightarrow{p}$ by the operator $\widehat{p} = -i\hbar\nabla$. The Hamiltonian operator is thus

$$\widehat{H} = \frac{1}{2m}\left(-i\hbar\nabla - e\overrightarrow{A}\right)^2 + V \tag{2.5}$$

Performing the square, this is equivalent to

$$\widehat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V + \frac{i\hbar e}{2m}\left(\nabla\cdot\overrightarrow{A} + \overrightarrow{A}\cdot\nabla\right) + \frac{e^2}{2m}\overrightarrow{A}\cdot\overrightarrow{A} \tag{2.6}$$

In the linear spectroscopy regime, the electromagnetic field is weak compared to the internal fields due to the charges that comprise the molecule. This allows to neglect the $\overrightarrow{A}\cdot\overrightarrow{A}$ term compared to the term in parentheses. The term in parentheses

can be cleaned up by noting that $\nabla \cdot \left(\overrightarrow{A}\Psi\right) + \overrightarrow{A} \cdot (\nabla\Psi) = 2\overrightarrow{A} \cdot (\nabla\Psi)$. Finally, the ∇ operator in terms of the particle momentum and write the Hamiltonian as the sum of a field-free zero-order term $\widehat{H}_0$ and a field-dependent perturbation operator $\widehat{H}', \widehat{H} = \widehat{H}_0 + \widehat{H'}$, where

$$\widehat{H}_0 = \frac{-\hbar^2}{2m}\nabla^2 + V \tag{2.7}$$

$$\widehat{H'} = \frac{-e}{m}\overrightarrow{A} \cdot \overrightarrow{p} \tag{2.8}$$

The point of $Eq.\,(2.8)$ is that the fundamental basis for spectroscopic transitions is the interaction of the momenta of charged particles with the vector potential of radiation.

2.3 Electromagnetic wave

2.3.1 Electromagnetic waves in free space

All electromagnetic field must satisfy all of MaxwellS. equations. In the free space outside the region, the charge and current densities are every-where zero, then MaxwellS. equations may be written in terms of E and H only as

$$\nabla \times H = \varepsilon_0 \frac{\partial E}{\partial t} \tag{2.9}$$

$$\nabla \times E = -\mu_0 \frac{\partial H}{\partial t} \tag{2.10}$$

$$\nabla \cdot E = 0 \tag{2.11}$$

$$\nabla \cdot H = 0 \tag{2.12}$$

By taking the curl of equations(2.9) and (2.10) can transform these first-order differential equations in to second-order equations, one can obtain

$$\nabla^2 E = \varepsilon_0 \mu_0 \frac{\partial^2 E}{\partial t^2} \tag{2.13}$$

$$\nabla^2 H = \varepsilon_0 \mu_0 \frac{\partial^2 H}{\partial t^2} \tag{2.14}$$

The velocity of electromagnetic wave is

$$c = \frac{1}{\sqrt[2]{\varepsilon_0 \mu_0}} \tag{2.15}$$

The electric and magnetic fields are vector quantities and therefore assume that the plan-wave solutions of equations (2.13) and (2.14) are of the form:

$$E\left(r,t\right) = \hat{e}_x E_0 e^{i(\omega t - kr)} \tag{2.16}$$

$$H\left(r,t\right) = \hat{e}_y H_0 e^{i(\omega t - kr)} \tag{2.17}$$

where $\hat{e}_x, \hat{e}_y$ are unit vectors, and E_0, H_0 are complex amplitudes.

The physical fields are obtained by taking the real part of the complex quantities.

2.3.2 Electromagnetic waves in medium

The electromagnetic state of matter at a given point is described by four equations:

1.the volume density of electric charge ρ

2. the volume density of electric dipoles, called the polarization P

3.the volume density of magnetic dipoles, called the magnetization M

4. the electric current per unit area, called the current density J

All of these quantities are considered to be macroscopically averaged in order to smooth out the microscopic variations due to the atomic makeup of all matter. They are related to the macroscopically averaged fields E and H by the following Maxwell equations:[32]

$$\nabla \times E = -\mu_0 \frac{\partial H}{\partial t} - \mu_0 \frac{\partial M}{\partial t} \tag{2.18}$$

$$\nabla \times H = \varepsilon_0 \frac{\partial E}{\partial t} + \frac{\partial P}{\partial t} + J \tag{2.19}$$

$$\nabla \cdot E = -\frac{1}{\varepsilon_0} \nabla \cdot P + \frac{\rho}{\varepsilon_0} \tag{2.20}$$

$$\nabla \cdot H = -\nabla \cdot M \tag{2.21}$$

If one introduces the abbreviation D for the quantity $\varepsilon_0 E + P$, known as the electric displacement, and the abbreviation B for $\mu_0 (H + M)$, called the magnetic

induction ,then Maxwell′s equations assume the more compact forms:

$$\nabla \times E = -\frac{\partial B}{\partial t} \tag{2.22}$$

$$\nabla \times H = \frac{\partial D}{\partial t} + J \tag{2.23}$$

$$\nabla \cdot D = \rho \tag{2.24}$$

$$\nabla \cdot B = 0 \tag{2.25}$$

The response of the conduction electrons to the electric field is given by the current equation (ohm′s law)

$J = \sigma E$ where σ is the conductivity.

The constitutive relation $D = \epsilon E$ describes the aggregate response of the bond charges to the electric field. The corresponding magnetic relation is $B = \mu H$

An alternate way to express the response of the bound charges is

$$P = (\epsilon - \varepsilon_0) E = \chi \varepsilon_0 E \tag{2.26}$$

which gives the proportionality between the polarization and the impressed electric field .

The proportionality factor

$\chi = \frac{\epsilon}{\varepsilon_0} - 1$, is known as the electric susceptibility

Optically linear medium are characterized by linear response of the medium to the electric field. Considering an alternating electric field at position r, which varies, sinusoidal with time $E(t) = E_0 \cos(\omega t)$. In the electric dipole approximation, the dielectric polarization $P(t)$ is created by local response in the medium.

$$P(t) = \varepsilon_0 \chi^{(1)} E_0 \cos(\omega t) \tag{2.27}$$

For optically medium $\nabla \cdot E = 0$,and applying the identity $\nabla \times \nabla \times E = \nabla(\nabla \cdot E) - \nabla^2 E$:

$$\nabla^2 E - \mu_0 \varepsilon_0 \left(\chi^{(1)} + 1\right) \frac{\partial^2 E}{\partial t^2} = 0 \tag{2.28}$$

For a wave propagating in $+z$-direction in a weakly absorbing medium:

$$E = E_0 \exp\left(-\frac{1}{2}\alpha z\right) \cos(\omega t - kz) \tag{2.29}$$

where α is the natural absorption coefficient and $k\,(k = 2\pi n/\lambda)$ is the magnitude of the wave vector. Both α and n represent the linear response of the medium and linked to the imaginary and real part of $\chi^{(1)}$:

$$\alpha = \frac{\omega \operatorname{Im}\left\{\chi^{(1)}\right\}}{c_0} \tag{2.30}$$

$$n = \sqrt{1 + \operatorname{Re}\left\{\chi^{(1)}\right\}} \tag{2.31}$$

The real and imaginary part of the susceptibility $\chi(1)$ are coupled through Kramers-Kronig relation:

$$\operatorname{Re}\left\{\chi^{(1)}(\omega_0)\right\} = \frac{2}{\pi} \int_0^{+\infty} d\omega \frac{\omega \operatorname{Im}\left\{\chi^{(1)}(\omega)\right\}}{\omega_0^2 - \omega^2} \tag{2.32}$$

2.4 The Absorption and Emission of Radiation

2.4.1 Time-dependent perturbation theory

Spectroscopy involves transition between states. To discuss transitions, the time-dependent Schrodinger equation is used.[33] Then to find an approximate solution to the time-dependent Schrodinger equation, in the case that the Hamiltonian can be expressed as the sum of a zero-order part $\hat{H}_0$ that does not depend on time, and a perturbation $\hat{H}^{'}$ that does [29] . The Schrodinger equation then takes the form

$$\left[\hat{H}_0 + \hat{H}^{'}(t)\left|\Psi\right\rangle = i\hbar\frac{\partial}{\partial t}\left|\Psi\right\rangle\right] \tag{2.33}$$

Let assume that the zero-order eigenfunctions and eigenvalues are known: $\hat{H}_0\left|n\right\rangle = E_n\left|n\right\rangle$, and using the zero-order wavefunctions $\Psi_n(0) \equiv \left|n\right\rangle$ as basis for expanding the perturbed wavefunction

$$\left|\Psi\right\rangle = \sum_n c_n(t)\, e^{-iE_n t/\hbar}\left|n\right\rangle \tag{2.34}$$

Eq.(2.34) presents the perturbed state as a superposition of the stationary states expressed in the Schrodinger representations phase factors $e^{-iE_n t/\hbar}$ and the coefficients $c_n(t)$ convey the time dependence of $\left|\Psi\right\rangle$

The coefficient $c_n(t)$ is given by the projection of the total wavefunction onto the n^{th} basis state:

$$c_n(t) = \left\langle\Psi(t)\right|\left.n\right\rangle e^{iE_n t/\hbar} \tag{2.35}$$

Using (2.34) to (2.33), one can have

$$\sum_n c_n(t)\, e^{-iE_n t/\hbar}\left(\hat{H}_0+\hat{H}'\right)|n\rangle = i\hbar\sum_n \frac{\partial}{\partial t}\left\{c_n(t)\, e^{-iE_n t/\hbar}|n\rangle\right\} \tag{2.36}$$

The sum runs over an infinite number of eigenstates indexed by the letter n.

Using a state m, multiply both sides of Eq.(2.36) by the complex conjugate of the wavefunction for state m, and then integrate over all space. The result is

$$\sum_n c_n(t)\, e^{-iE_n t/\hbar}\left\{\left\langle m\left|\hat{H}_0\right|n\right\rangle + \left\langle m\left|\hat{H}'\right|n\right\rangle\right\} = i\hbar\sum_n \frac{\partial}{\partial t}\left\{c_n(t)\, e^{-iE_n t/\hbar}\langle m \mid n\rangle\right\} \tag{2.37}$$

The eigenfunctions are orthonormal: $\langle n \mid m\rangle = \delta_{nm}$; so in the infinite sum on the right-hand side, only the term $n = m$ survives. And since $\left\langle n\left|\hat{H}_0\right|m\right\rangle = E_m\delta_{nm}$, the first sum on the left-hand side is similarly reduced to one term. Thus

$$c_m(t)\, e^{-iE_m t/\hbar}E_m + \sum_n c_n(t)\, e^{-iE_n t/\hbar}\left\langle m\left|\hat{H}'\right|n\right\rangle = i\hbar\frac{\partial c_m}{\partial t}e^{-iE_m t/\hbar} + i\hbar\left(\frac{-iE_m}{\hbar}\right)e^{-iE_m t/\hbar}c_m(t) \tag{2.38}$$

where $V_{mn}(t) = \left\langle m\left|\hat{H}'(t)\right|n\right\rangle$ and $\omega_{nm} \equiv (E_n - E_m)/\hbar = -\omega_{mn}$

Let the perturbation $\hat{H}'(t)$ act from $t = 0$ to $t = t_1$. taking the definite integral of (2.38), to give

$$c_f^{(1)}(t) = \frac{-i}{\hbar}\int_0^{t_1} dt' e^{i\omega_{fi}t'}\left\langle m\left|\hat{H}'\left(t'\right)\right|n\right\rangle \tag{2.39}$$

$$c_f^{(1)}(t) = \frac{-i}{\hbar}\int_0^{t_1} dt' e^{i\omega_{fi}t'}V_{fi}\left(t'\right) \tag{2.40}$$

2.4.2 Perturbation due to Electromagnetic Radiation

Eq.(2.8) applies to any problem involving a perturbation that varies in time . But in case when $\mathrm{V}_{fi}(t)$ is due to time-varying electromagnetic field, the time-dependent operator is

$$\hat{H}'(t) = \frac{ie\hbar}{m}\overrightarrow{A}\cdot\nabla = -\frac{e}{m}\overrightarrow{A}\cdot\overrightarrow{P} \tag{2.41}$$

Where P is the momentum, m is the mass and A is the vector potential.The vector potential is written as follows:

$$\overrightarrow{A} = \frac{A_0}{2}\left[e^{i(k\cdot r-\omega t)} + e^{-i(k\cdot r-\omega t)}\right] = \mathrm{Re}\,\overrightarrow{A_0}e^{i(k.r-\omega t)} \tag{2.42}$$

The primary mechanism for the interaction of light and matter is due to the operator $\hat{H}'(t) = -\mu\cdot E(t)$, corresponding to energy of a dipole in a time - varying, but spatially constant, electric field . In Eq.(2.42) $k\cdot r \approx 2\pi r/\lambda << 1$ over the typical dimensions of a molecule, the exponential function can be expanded about $k\cdot r = 0$

$$e^{ik\cdot r} \approx 1 + (ik\cdot r) + \frac{1}{2}(ik\cdot r)^2 + \cdots \tag{2.43}$$

Using the first term of Eq.(2.43) :

$$V_{fi}(t) = \frac{ie\hbar}{m}\,\mathrm{Re}\left(e^{-i\omega t}\right)\langle f\,|A_0\cdot\nabla|\,i\rangle \tag{2.44}$$

$(k \longrightarrow 0$ limit)

Suppose that the vector potential points in the z direction. The relevant matrix element is then

$$V_{fi}(t) = \frac{ie\hbar A_0}{m}\,\mathrm{Re}\left(e^{-i\omega t}\right)\left\langle f\left|\frac{\partial}{\partial z}\right|i\right\rangle \tag{2.45}$$

where

$$i\hbar \left\langle f \left| \frac{\partial}{\partial z} \right| i \right\rangle = - \left\langle f \left| p_z \right| i \right\rangle \tag{2.46}$$

with the help of the commutator relation $[z, p_z] = i\hbar$ one can prove

$$p_z = \frac{im}{\hbar} \left(\hat{H}_0 z - z \hat{H}_0 \right) = \frac{im}{\hbar} \left[\hat{H}_{0,} z \right] \tag{2.47}$$

Then the matrix element is

$$\left\langle f \left| p_z \right| i \right\rangle = \frac{im}{\hbar} \left\{ \left\langle f \left| \hat{H}_0 z \right| i \right\rangle - \left\langle f \left| z \hat{H}_0 \right| i \right\rangle \right\} = im \frac{(E_f - E_i)}{\hbar} \left\langle f \left| z \right| i \right\rangle = i\omega_{fi} \left\langle f \left| z \right| i \right\rangle \tag{2.48}$$

Since the z component of the dipole moment operator is $\mu_z = -ez$, the matrix element can be written

$$V_{fi}(t) = -\frac{e}{m} \operatorname{Re}\left(e^{-i\omega t}\right) \left\langle f \left| A_0 \cdot p \right| i \right\rangle = i\omega_{fi} \operatorname{Re}\left(e^{-i\omega t}\right) \left\langle f \left| A_0 \cdot \mu \right| i \right\rangle \tag{2.49}$$

Switching from the vector potential to the electric field, with the relationship $E_0 = -\omega A_{0,}$and putting $\operatorname{Re}\left[\exp\left(-i\omega t\right)\right] = \frac{1}{2}\left[\exp\left(-i\omega t\right) + \exp\left(i\omega t\right)\right]$ one can get

$$V_{fi}(t) = -\frac{i\omega_{fi}}{2\omega} \left(\mu_{fi} \cdot E_0\right) \left(e^{i\omega t} + e^{-i\omega t}\right) \tag{2.50}$$

where the matrix element $\left\langle f \left| \mu \cdot E_0 \right| i \right\rangle = \left(\mu_{fi} \cdot E_0\right)$

Using the matrix element given in Eq.(2.50) in (2.40) leads to two integrals of the type

$$\int_0^t e^{i\left(\omega_{fi} \pm \omega\right)t'} dt' = \frac{i\left[e^{\left(\omega_{fi} \pm \omega\right)t} - 1\right]}{\omega_{fi} \pm \omega} \tag{2.51}$$

The coefficient of the state f at time t is thus

$$C_f^{(1)}(t) = \frac{i\omega_{fi}}{2\hbar\omega} \left(\mu_{fi} \cdot E_0\right) \left[\frac{e^{i\left(\omega + \omega_{fi}\right)t} - 1}{\omega + \omega_{fi}} - \frac{e^{-i\left(\omega - \omega_{fi}\right)t} - 1}{\omega - \omega_{fi}} \right] \tag{2.52}$$

Suppose that $\omega \approx \omega_{fi}$, neglect the first term and square the second to get the probability of the $i \longrightarrow f$ transition.

$$P_{fi}(t) = \frac{\omega_{fi}^2 \left|\left(\mu_{if} \cdot E_0\right)\right|^2}{4\hbar^2\omega^2} \frac{\sin^2\left(\frac{\Delta\omega t}{2}\right)}{\left(\frac{\Delta\omega}{2}\right)^2} \tag{2.53}$$

where $\Delta\omega \equiv \omega - \omega_{fi}$ is the difference between the frequency of light and that of the transition

The properties of the function

$$f(t, \Delta\omega) \equiv \frac{\sin^2\left(\frac{\Delta\omega t}{2}\right)}{\left(\frac{\Delta\omega}{2}\right)^2} \tag{2.54}$$

using the integral

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \pi \tag{2.55}$$

Using the Fermi$'$s Golden Rule $f(t, \Delta\omega) \Longrightarrow 2\pi t\delta(\omega - \omega_{fi})$, gives a transition probability that is linear in time:

$$P_f(t) = \frac{2\pi \left|\left(\mu_{if \cdot E_0}\right)\right|^2 t}{4\hbar^2} \delta(\omega - \omega_{fi}) \tag{2.56}$$

The significance of this result is that the transition rate ω_{if}, which is the transition probability per unit time, is independent of time.

$$\omega_{if} = \frac{p_f(t)}{t} = \frac{\left|\left(\mu_{if} \cdot E_0\right)\right|^2}{4\hbar^2} \left[\delta(\nu - \nu_{fi}) + \delta(\nu + \nu_{fi})\right] \tag{2.57}$$

The second delta function in the above expression results from adding in the contribution of stimulated emission.The substitution $\delta(\nu - \nu_{fi}) = 2\pi\delta(\omega - \omega_{fi})$ has been made. Using the practical applications of the Golden Rule, for the energy density of monochromatic radiation, by replacing the square of the amplitude

of the electric field in Eq.(2.53) by making the correspondence $u(\nu) = \frac{1}{2}\varepsilon_0 E_0^2 \Longleftrightarrow \int \rho(\nu)\, d\nu$, and integrating over all frequencies. The result is

$$\omega_{if} = \frac{P_f(t)}{t} = \frac{\left|\mu_{if} \cdot \hat{e}\right|^2 \rho(\nu_{fi})}{2\varepsilon_0 \hbar^2} \tag{2.58}$$

where $\hat{e}$ is a unit vector in the direction of the electric field. The x, y, and z components of the transition moment squared must be equal, $\left|\mu_{if}\right|^2 = 3\left(\mu_{if}\right)_x^2$ to get

$$\omega_{if}(t) = \frac{\left|\mu_{if}\right|^2 \rho(\nu_{fi})}{6\varepsilon_0 \hbar^2} \tag{2.59}$$

2.4.3 Comparison of rate of probability with experimental quantities

By comparing the transition rate in the Einstein picture to the quantum mechanical transition rate given by the Golden Rule, one form of the Golden Rule, convenient when absorption is being considered, was found to be [29] .

$$\omega_{if} = \frac{\left|\mu_{if}\right|^2 \rho(\nu_{fi})}{6\varepsilon_0 \hbar^2} \tag{2.60}$$

This is a transition rate per molecule, so on multiplying by the number of molecules in the initial state, gives the total transition rate

$$N_i \omega_{if} = N_i B_{if}\, \rho(\upsilon_{fi}) \tag{2.61}$$

Thus the Einstein rate is the same as that given by the Golden Rule if

$$B_{if} = \frac{\left|\mu_{if}\right|^2}{6\varepsilon_0 \hbar^2} \tag{2.62}$$

The differential form of Beer′s law can be written in terms of the molar absorptivity $\epsilon(\nu)$ as follows:

$$-dI = 2.303\epsilon(\nu) CIdl \tag{2.63}$$

The molar absorptivity is generally expressed in units of $L\ mol^{-1}\ cm^{-1}$, so the concentration C is in mol/L and the path length l in cm. The factor of 2.303 in Eq.(2.63) is derived from the form of Beer′s law preferred by spectroscopists $I = I_0 10^{-\epsilon Cl}$

If N is the number of molecules per cm^3 in the initial state i, then an other way to write Eq.(2.63) is

$$-dI = Nh\nu\omega_{fi}dl \tag{2.64}$$

equating Eqs. (2.63) and (2.64) gives the transition rate per molecule as

$$\omega_{fi} = \frac{2.303\epsilon(\nu) CI}{Nh\nu} \tag{2.65}$$

It is convenient to replace the intensity I by $c_0 u$ and the molar concentration C by N/N_A , where c_0 is speed of light, N is the number of molecules per cm^3 and N_A is Avogadro′s number:

$$\omega_{fi} = \frac{2.303c_0\epsilon(\nu) u(\nu)}{N_A h\nu} \tag{2.66}$$

The total transition rate ought to be integrated over the band, replacing $u(\nu)$ by $\int \rho(\nu) d\nu$ and including $\epsilon(\nu)/\nu$ in the integrand:

$$\omega_{fi} = \frac{2.303c_0}{N_{Ah}} \int_{band} \frac{\rho(\nu)\epsilon(\nu)}{\nu} d\nu \tag{2.67}$$

If the bandwidth of the source $\rho(\nu)$ is broad compared to the range of frequencies for which $\in(\nu)$ is significant, one can take $\rho(\nu) \approx \rho(\nu_{fi})$ to be constant. this gives a transition rate which can be directly compared to $B_{fi}\rho(\nu_{fi})$, and one obtain

$$B_{fi} = \frac{2.303c_0}{N_A h}\int_{band}\frac{\in(\nu)}{\nu}d\nu \tag{2.68}$$

Using $Eq.(2.63)$ one can get an equation which relates the square of transition moment to the integrated intensity:

$$\left|\mu_{if}\right|^2 = \frac{6\varepsilon_0\hbar^2(2.303c_0)}{N_A h}\int_{band}\frac{\in(\nu)}{\nu}d\nu \tag{2.69}$$

$Eq.(2.69)$ shows how the integrated molar absorptivity can be used to find the absolute value of the transition moment. In typical application of this expression , i and f are the ground and first excited electronic states, and the width of the absorption band results from a progression of vibrational transitions within a single electronic transition.

The integral in the right part of $Eq.(2.69)$ is called integral absorption I_A:

$$I_A = \int_{band}\frac{\in(\nu)}{\nu}d\nu = \frac{N_A h\left|\mu_{if}\right|^2}{(6\varepsilon_0\hbar^2)\,2.303c_0} = \frac{1}{3}S\left|\mu_{if}\right|^2 \tag{2.70}$$

with $S = \frac{N_A h}{2\varepsilon_0\hbar^2(2.303)c_0}$

2.5 UV-Visible Absorption spectra

The visible region of the spectrum comprises photon energies of 36 to 72 $kcal/mole$, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 $kcal/mole$. Ultraviolet radiation having wavelengths less than 200 nm is difficult to

handle, and is seldom used as a routine tool for structural analysis.

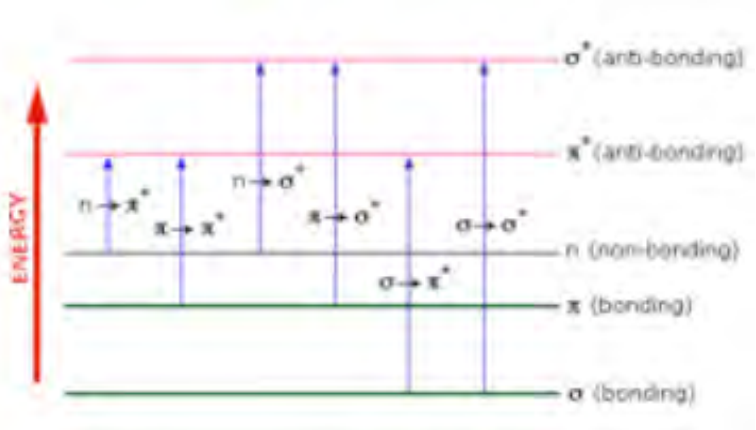

Fig. 2.1 energy spectra

The energy noted above are sufficient to promote or excite a molecular electron to a high energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "$electronic\ spetroscopy$". Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum.

For molecules that possess π bonding as in alkenes, alkynes, aromatics, acyl compounds of nitrites, energy that is available can promote electrons from a π bonding molecular orbital to a π anti-bonding molecular orbital. This is called a $\pi^* \longleftarrow \pi$ transition. The energy difference for such a transition to occur will depend upon the atoms π bonded to each other, other atoms attached as well as the relationship between two or more π bonds within the molecule. π bonds between two carbon atoms will have a different $\pi^* \longleftarrow \pi$ transition compared to π bonds between a carbon and an oxygen atom ($a\ carbonyl$) or a π bond between a carbon atom and a nitrogen

atom (in a nitrile) . This is because there will be a different energy gap between the π bonding and π anti-bonding molecular orbital energy states. The greater the energy of transition the shorter is the wavelength of UV or Visible radiation will have to be for electrons to be promoted from the bonding to the anti-bonding state.Every group of atoms with π bonding will have a different wavelength where maximum absorption will take place.This is called the $\lambda_{\max}$ the wavelength where maximum absorption takes place, and the group of atoms with the π bonding is called a $"chromophore"$. Each chromophore will have a different energy of transition between the bonding and anti-bonding molecular orbitals for which the electron transition takes place.

2.6 Thermal properties

Thermogravimetric analysis(TGA) is an analytical technique used to determine a material$'$s thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon,and the weight is recorded as a function of increasing temperature. Sometime, the measurement is performed in a lean oxygen atmosphere (1 to 5% O_2 in N_2 or He) to slow down oxidation [34] .

One of the first important applications of thermogravimetry was the determination of correct drying temperatures for precipitates used in gravimetric analysis. A second important application was the identification of the gases given off while a

sample′s temperature is increased. In addition, the composition of the residue can be determined. This information reveals the chemical decomposition process of heated materials and permits identification of the formulas of the residue.

A third application of TGA is the identification of the compounds present in mixtures of materials [35] .

A technique in which the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.

The DTA curve is generally a plot of the difference in temperature (ΔT) as the ordinate against the temperature T (or occasionally,time) as the abscissa.

Chapter 3
Materials and Methods

In this unit, laboratory apparatus, instruments, chemical and experimental procedures will be presented.

3.1 Apparatus and Instruments

The labolatory apparatus used for the experimental are beakers, measuring cylinders, spatula, quartz cuvette, funnel, separator funnel, glass filter, magnetic stirrer with hot plate, and 250 μm sieve. The instruments used for the experiment are electronic balance for measuring mass of roasted and ground coffee (SA120, number 1450, graduated with a division of 10^{-2} gm level, Boulder company),Electronic micro balance for measuring mass of caffeine (M5.3A, Sauter company), Electric motor grinder for grinding green coffee beans, Electric motor grinder for grinding roasted coffee beans,$(probat - werke)$ stove to roast green coffee beans, Electronic balance for measuring green and roasted coffee beans, double beam Uv|vis spectrometer with model Uv/vis/NIR spectrometer Lambda 19 ,wavelength range $170\ nm - 3200\ nm$, wavelength accuracy $0.1\ nm$ and slit width $1\ nm$ or $2\ nm$ as required. The spectrometer was interfaced with personal computer which is operated by software uvcss.

3.2 Chemicals

The chemicals used for the experiment are: dichloromethane (99.6% A.C.S reagent , ALDRICH) and de-ionized water.

3.3 Samples

In this investigation , three different types of samples were used, pure caffeine from (Evan pharmaceutical company, England), ground raw coffee, and roasted and ground coffee samples from (Sidama) collected from Ethiopian coffee and tea quality and liquoring center.

3.4 Method of the experiment

3.4.1 Sample preparation

A coffee arabica sample from Ethiopia (Sidamo) were subjected to two different protocols of roasting in (PROBAT-WERKE) stove. The first protocol was carried out at constant time $(6\,\mathrm{min})$ and different temperatures ranging from $140 - 220^0c$ were applied and the second one was was performed at constant temperature (180^0c) with variation of the exposure time from $(5 - 10\,\mathrm{min})$.The mass of green coffee bean in each protocol was $100\ g$. All samples were grounded and screened through 250 μm mesh sieve immediately before sample analyses and moisture determination.

3.4.2 Calibration of the experiment

To determine the percentage of caffeine in different roasted and ground coffee it is necessary to set up calibration using pure caffeine. For calibration, pure caffeine and de-ionized water as a solvent were used . The procedures for calibration are:

1. A pure caffeine is weighted using electrical balance graduated at a microgram level.

2. de-ionized water is weighted using electrical balance graduated at microgram level .

3. A pure caffeine dissolved in de-ionized water and stirred for $10\,\mathrm{min}$. using magnetic stirrer.

Using the data collected from step (1) $-$step(3) the number of moles are determined by:

Number of moles = $\frac{actual\ weight\ of\ \ caffeine}{Molecular\ weight\ of\ caffeine}$

and the concentration C is:

Concentration = $\frac{Number\ of\ moles}{Volm\ of\ de-ionized\ water}$

The absorption spectrum of this solution was undertaken using UV/Vis spectrophotometer similarly the experiment is repeated for different concentrations and the absorption spectrum of these concentrations were collected. Then from the graph absorbance versus concentration, the molar decadic absorption coefficient was determined using Beer′s law.

3.4.3 Quantitative analysis

Qualitative measurements involve the use of Beer−Lambert law , and a calibration graph of absorbance versus concentration should be a straight line of gradient $(\varepsilon\iota)$ (molar absorptivity times the path length) $[29]$. The gradient $(\varepsilon\iota)$ value can be determined from different prepared concentrations, because in any real experiment there will be random errors arising from the limitation of the measurement . If there is a sufficiently large number of experimental points and one has reason to believe that the deviation of these points from a straight line can be attributed to random errors, a better value may be obtained by minimizing the squares of the deviations from the "straight line" values.

In the equation $A = \varepsilon C\ell$, the value of concentrations are known. The deviation of experimental values from the equation may then be written $A - \varepsilon C_i\ell = ei$ .The deviations ei , are squared and the sum of them taken for all the experimental points.It is required that this sum of the squares of the deviations by a minimum. This is achieved by setting the derivative with respect to the adjustable parameter, ε or $\varepsilon\ell$, equal to zero.

$$\frac{\partial \sum_i e_i^2}{\partial \varepsilon\ell} = \frac{\partial \sum_i \left[A_i^2 - 2\varepsilon\ell C_i A_i + (\varepsilon\ell C)^2\right]}{\partial \varepsilon\ell} = 2\sum \left(\varepsilon\ell C_i^2 - C_i A_i\right) = 0 \qquad (3.1)$$

The gradient $(\varepsilon\ell)$ is therefore

$$\varepsilon\ell = \frac{\sum_i A_i C_i}{\sum C_i^2} \qquad (3.2)$$

To find the best value of the absorptivity one should therefore multiply each absorbance value by its corresponding concentration and find the sum of these products. The sum is divided by the sum of the squares of the concentrations.

3.5 setting up experimental procedure

To determine the caffeine concentration in roasted and ground coffee in water solution two main experimental procedures are necessary.

1. Procedure to determine the absorbance of the spectrum of caffeine extracted from roasted and ground coffee dissolved in de-ionized water.

2. procedure to determine the absorbance of the spectrum of roasted and ground coffee in water solution.

3.5.1 Experimental procedure for the determination of caffeine content from roasted and ground coffee solution using extraction method

In this experimental procedure , caffeine is extracted from each solutions.

1.A coffee sample from local source were subjected to two different protocols of roasting in $(PROBAT - WERKE)$ stove.

2. The first protocol was carried out at constant time $(6\,\mathrm{min})$ and different temperatures , ranging from $140 - 220^0 c$.

3. The second protocol was performed at constant temperature $200^0 c$, with variation of the exposure time $4 - 10\,\mathrm{min}$.

4. All samples were grounded and screened through a $250\ \mu m$ sieve.

5. A $50\ mg$ portion of each grounded coffee is added to $30\ ml$ of de-ionized water.

6. Each solutions of roasted and ground coffee is stirred by magnetic stirrer with hot plate for an hour.

7. The solutions were filtered through a glass filter.

8. Each filtered solution is added to $20ml$ of dichloromethane and stirred for $10\,\mathrm{min}$.

9. The above mixture is added to a separator funnel. Due to density difference dichloromethane with the extracted caffeine is easily separated from coffee in water solution.

10. The above steps $(7-8)$ are repeated three times.

11. The volume of dichloromethane with extracted caffeine in measuring cylinder is measured and the result will be recorded .

12. Using uv/vis spectrophotometer the absorption spectra of each solution of extracted caffeine are collected.

3.5.2 Procedure to determine the absorbance of roasted and ground coffee in de-ionized water

In this experimental procedure sieved roasted and ground coffee and de-ionized water are used: The procedures are:

1. Roasted and ground coffee were screened by $250\ \mu m$ sieve.

2. $50\ mg$ of sieved roasted and ground coffee from each sample is measured and added to $60\ ml$ of de-ionized water.

3. The solution of each roasted and ground coffee powder is stirred by magnetic stirrer for an hour.

4. Each solution is filtered using glass filter. The filtered solution is measured by measuring cylinder.

Finally using uv/vis spectrophotometer the absorption spectra of each solution are collected.

The physical quantities measured in this experiment are the absorption spectra of roasted and ground coffee in water solution and the absorption spectra of caffeine extracted from these solutions. The other quantities like concentration of caffeine, molar decadic absorption coefficient of caffeine,translational dipole moment of caffeine, and the average integrated area under the curve are calculated from these measured values using equations (3.1) , (2.69) ,and (2.70) .

Chapter 4
Results and Discussion

Based on the experimental procedures and measurements described in the previous section the results obtained are presented in this unit.

4.1 Absorbance versus concentration relation of pure caffeine

To determine the transition property of caffeine in water solution, different concentration of pure caffeine were prepared and absorption spectra are recorded using UV/VIS spectrophotometer. The peak absorbance of each concentration of the absorption spectra of pure caffeine in water solution is at peak wavelength of $271.6nm$

The absorbance versus wavelength graph of the absorption curve for different concentration of pure caffeine is shown in Fig. 4.1.

From the measured value of absorbance and concentration of pure caffeine, the value of molar decadic absorption coefficient (ε) , transition dipole moment $\left(\mu_{eg}\right)$ and integral absorption (I_A) were determined. The summarized value is shown in table 4.1.

table 4.1 physical quantities of absorption spectra of different concentrations of pure caffeine

A	C$\left(\frac{mol}{m^3}\right)$	$\varepsilon\left(\frac{m^2}{mol}\right)$	$\mu_{fi(cm)\times 10^{-30}}$	$I_A\left(\frac{m^2}{mol}\right)$
1.0567	0.10299	1026	12.37	149.79
0.5947	0.051495	1154	13.84	187.43
0.3595	0.03433	1047	12.38	149.9
0.2210	0.02575	1052	12.53	153.54

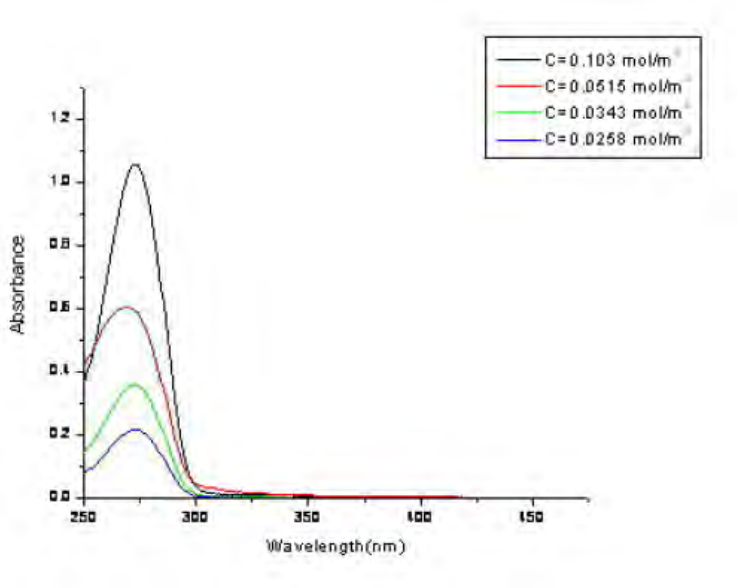

Fig. 4.1 Absorbance versus wavelength graph for different concentration of pure caffeine

The value of molar decadic absorption coefficient of pure caffeine in water solution using equation(3.1) is $1054\ m^2/mol$. Similarly the value of transition moment using equation (2.69) is$(12.78 \pm 0.71) \times 10^{-30}$ Cm. The average integrated area under the curve is $(160.165)\ m^2/mol$.In electronic spectroscopy specially in organic molecules the transition observed in UV/VIS region is $\pi^* \longleftarrow \pi$. Then for pure

caffeine the electronic type transition is $\pi^* \longleftarrow \pi$ transition and this transition is the cause for absorption.

The concentration versus absorbance graph for the quantities described in able 4.1 is shown in Fig.4.2.

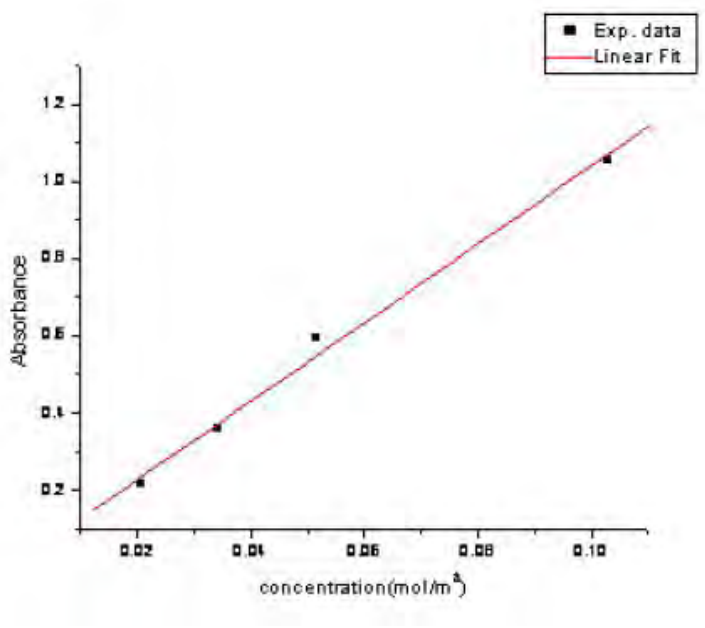

Fig.4.2 Absorbance versus concentration relation of pure caffeine

4.2 Evaluation of weight loss of green coffee during roasting

A lab-scale cylindrical coffee roaster (PROBAT-WERKE) coupled to a gas condensation was prepared for the purpose of roasting in the ECTQLC. The roaster was

pre-heated until the available temperature reached, and then loaded with $100\ gm$ green washed coffee for each roasting time and degree of roast as shown in table 4.2

Table 4.2 Roasting characteristics of the coffee used

T_0 before roasting(^0c)	T during roasting(^0c)	roasting time($\min$)	total roast loss($\%$)
170	162-170	6	10.5
180	170-172	6	12.6
190	180-181	6	15.5
210	190-194	6	16.7
240	198-200	6	17.3
250	202-205	6	20.4
220	200	4	7.5
220	200	5	11.8
220	200	6	14.9
220	200	7	21.7
220	200	8	28.8

During roasting the initial temperature decreases due to the removal of water from the green coffee. According to [37] roasting procedure of coffee involves on initial step during which the contained water in beans is removed, after such step the real roasting is initiated.

The weight loss curve ($Figure\ 4.3$) presents a behavior similar to that reported in the literature [19], occurring at two rates. The weight loss during the first $4\,\min$ is due to the slow release of water and volatile compounds. The increase in weight loss after that time can be attributed to an intensive release of organic compounds and co_2 during pyrolysis. The onset of pyrolysis can be associated with the transition between the two slops. According to the reviewed literature, transition should occur at about 10% weight loss [39].In this case, transition occurred at approximately 7.5 $\%$.

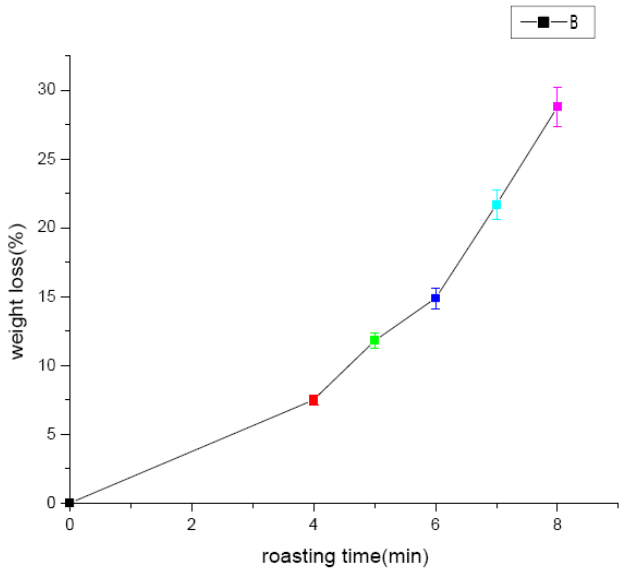

Fig. 4.3 weight loss

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The rate constant(K_T) for the thermochemical reactions in roasted coffee at 200^0c were calculated from the slope of weight loss in coffee versus time data $(4-5\,\mathrm{min})$. The result is $K_T = -0.0651$.

4.3 Effect of Roasting Time on the content of caffeine in coffee

In this section the concentration and % caffeine in roasted and ground coffee of different samples, which are performed at constant temperature $(170^0c, 180^0c$ and $200^0c)$ with variation of exposure time from $(4-10\,\mathrm{min})$ were investigated.

The coffee samples were prepared based on the roasting protocol and experimental procedures described in the previous sections extraction techniques could not

completely remove the possible interferences with caffeine spectra, then the interfering matrix element is removed by fitting it with Gaussian model.

The samples were roasted at constant temperature (170^0c) with variation of exposure time from $4-10\,\mathrm{min}$ .The results of the measurement are shown in figure 4.4.

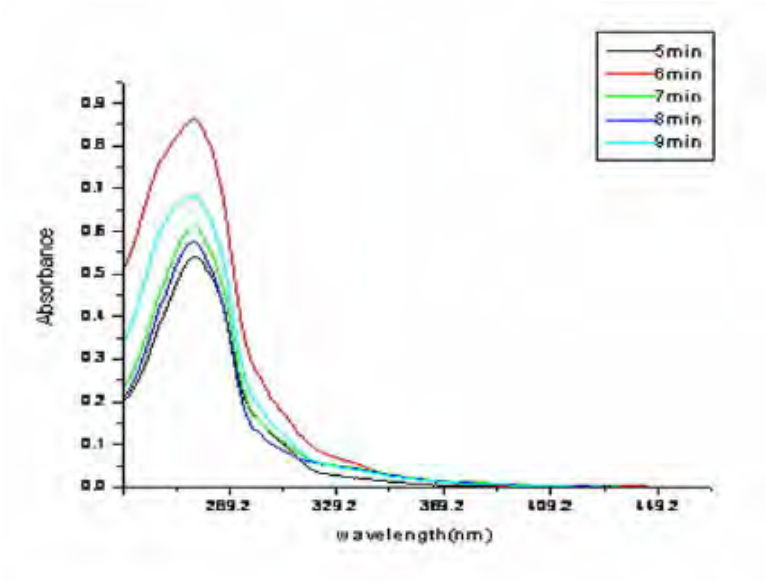

Fig 4.4 Absorption spectra of caffeine at 170^0c degree of roast with variation of exposure time $(5-9\,\mathrm{min})$

From the absorption spectra one can observe an increase and decrease in caffeine concentration as a function of roasting time.The absorption maximum wavelength observed was the same $(276.4nm$ through out$)$. All the important parameters are summarized in table 4.4.

Table 4.4 parameters of caffeine extracted from R/G coffee at 170^0c with variation of exposure time.

roasting time$(\min)$	$\lambda_{\max}$	$A_{\max}$	$m_i\ (coffee)$ in mg	C $\left(\frac{mol}{m^3}\right)$	% of caffeine
Green	275.6	0.3292	51.1	0.0312	0.725
5	276.4	0.5407	50.9	0.0513	1.07
6	276.4	0.8649	50.6	0.0821	1.69
7	276.4	0.6111	50.2	0.058	1.28
8	276.4	0.5754	50.2	0.0546	1.24
9	276.4	0.6823	50.2	0.0647	1.63

From table 4.4 the graph of % of caffeine versus roasting time at constant temperature (170^0c) are shown in figure 4.5.

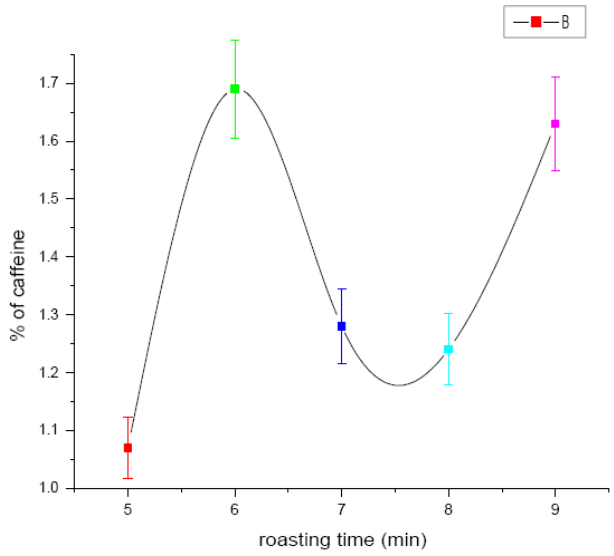

Fig. 4.5 Experimental influence of the time of roast at 170^0c

The caffeine content $(Fig.4.5)$ shows an increase up to $6\,\min$ of roasting. As [19] the weight of the green beans reduced by up to 20% or more $(say\ 10\%\ water,\ 10\%\ dry\ matter)$ during roasting, the actual percentage amount of caffeine may increase by up to 10% on a dry roasted basis. For an exposure time greater than $6\,\min$ a gradual decrease

of the caffeine content was observed. It would be expected that caffeine decomposes might have occurred to a higher extent when its decomposition temperature reached 185^0c. In this case the decomposition occurs around $6\,\mathrm{min}$.

Similarly using the same roasting protocol and experimental procedures for 180^0c constant temperature with different exposure time from $4-8\,\mathrm{min}$ the absorption spectra are shown in $Fig\ 4.5$.

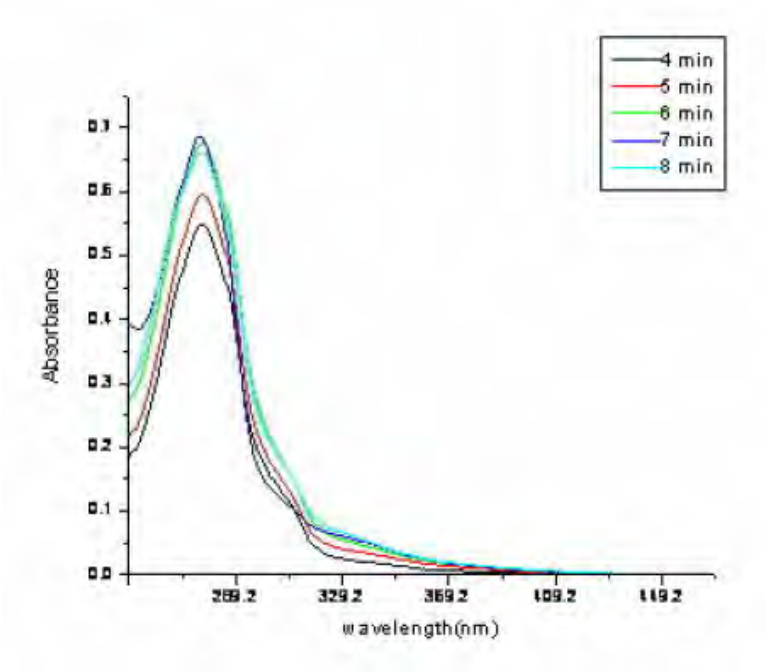

Fig. 4.6 Absorption spectra of caffeine at 180^0c

degree of roast with variation of exposure time $(4-8\,\mathrm{min})$

The absorbance of the absorption spectra at a peak wavelength, concentration and % of caffeine extracted from roasted and ground coffee at constant temperature (180^0c) with variation exposure time are shown in table 4.5

Table 4.5 parameters of caffeine extracted from roasted and ground coffee at 180^0c with variation of exposure time.

roasting time$(\min)$	$\lambda_{\max}$	Abs.	m$_i$ $(coffee)$	conc.$\left(\frac{mol}{m^3}\right)$	% of caffeine
green	275.6	0.3292	51.1	0.0312	0.725
4	277.2	0.5491	50.7	0.0521	1.097
5	277.2	0.596	50.2	0.0565	1.181
6	277.2	0.675	50.3	0.064	1.36
7	275.6	0.687	50.1	0.0652	1.54
8	276.4	0.661	50.5	0.0627	1.205

From table 4.5 the graph of % of caffeine versus roasting time at constant temperature (180^0c) are shown in figure 4.7.

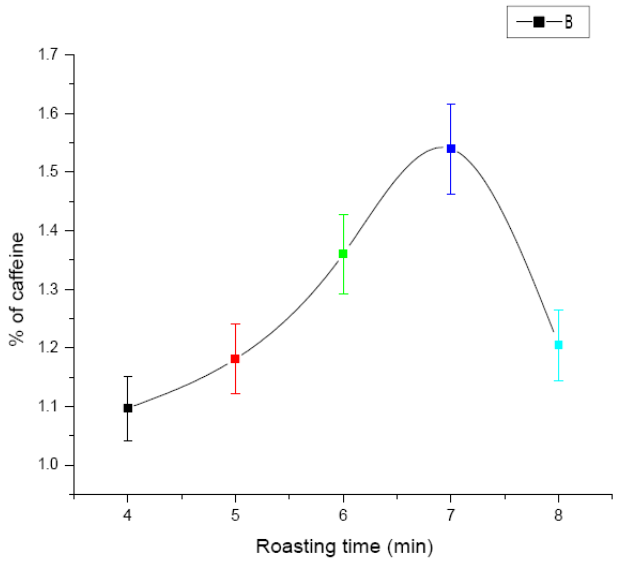

Fig.4.7 Experimental influence of the time of roast at 180^0c

The caffeine content increased up to $7\,\min$ of heating. For an exposure time greater than $7\,\min$ a gradual decrease of the caffeine content was observed. For this constant temperature caffeine decomposition occurs around $7\,\min$. The absorption maximum wavelength observed varies between $275.6 - 277.2\ nm$.

Finally for 200^0c constant temperature with variation of exposure time from $4-8\,\mathrm{min}$ the absorption spectra are described in figure 4.7.

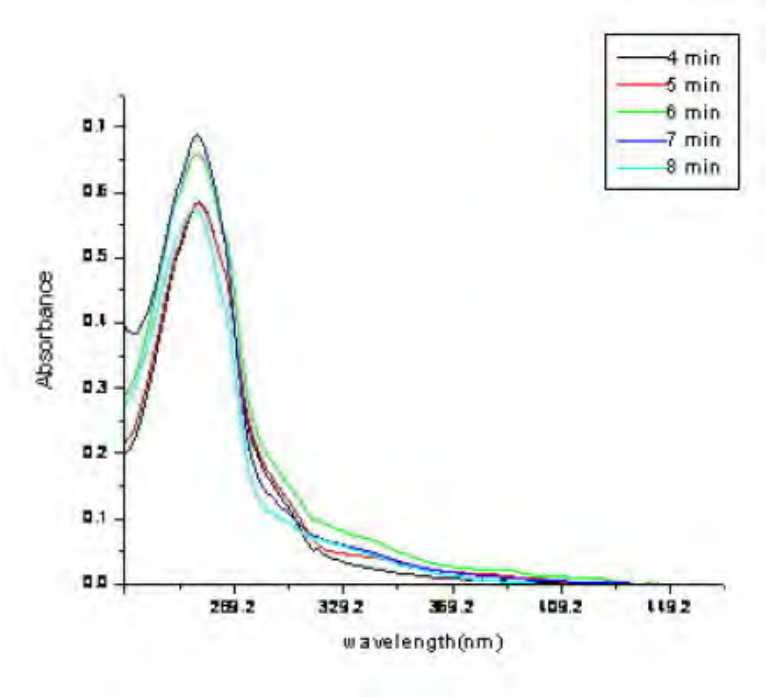

Fig 4.8 Absorption spectra of caffeine at 200^0c with different exposure time $(4-8\,\mathrm{min})$

Similarly as observed for 180^0c degree of roast, there is an increase and decrease of caffeine concentration as function of roasting time. The absorption maximum wavelengths observed varies between $274.8-276.4\ nm$. Important parameters are summarized in table 4.6

Table 4.6 different parameters of caffeine extracted from R/G coffee at 200^0c temperature with variation of exposure time.

roasting time(min)	$\lambda_{\max}\,(nm)$	Abso.	$m_i\,(coffee)$	conc.$\left(\frac{mol}{m^3}\right)$	% of caffeine
green	275.6	0.3292	51.1	0.0312	0.725
4	276.4	0.5849	50.1	0.0555	1.14
5	276.4	0.5834	51.1	0.0535	1.188
6	276.4	0.6615	50.2	0.0628	1.34
7	275.6	0.6871	50.1	0.0652	1.39
8	274.8	0.5753	50.3	0.0546	1.075

The graph of % of caffeine versus roasting time at 200^0c are shown in figure 4.8.

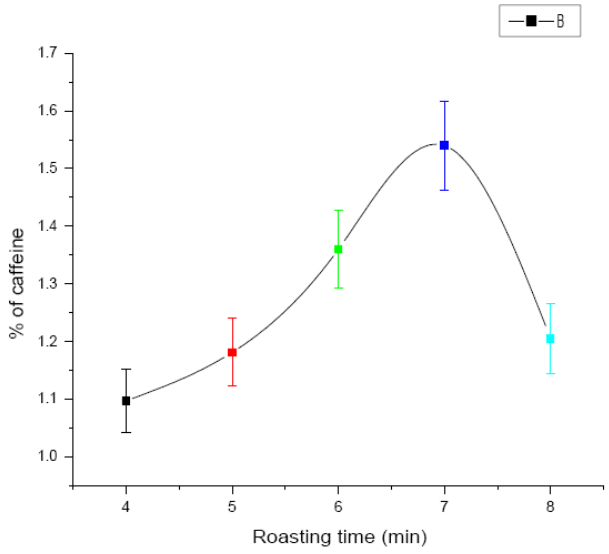

Fig.4.9 Experimental influence of roasting time at 200^0c

The caffeine content $(Fig.4.9)$ shows similar trend as $(Fig.4.8)$,there is an increase in caffeine content up to $7\,\mathrm{min}$ of heating. For the exposure time greater than $7\,\mathrm{min}$ a gradual decrease of caffeine content was observed. In this case the decomposition of caffeine occurs around $7\,\mathrm{min}$ of exposure time.

4.4 Effect of roasting temperature on the content of caffeine in coffee

In this part the content of caffeine in roasted and ground coffee of different samples, which are performed at constant time $(6\,\mathrm{min})$ and several temperatures were investigated.The coffee samples were prepared based on the roasting protocol and experimental procedures described in the previous sections results of the roasting trial conducted at constant time $(6\,\mathrm{min})$ and several temperatures are presented in table 4.2. The results of the measurements are shown in Fig. 4.10.

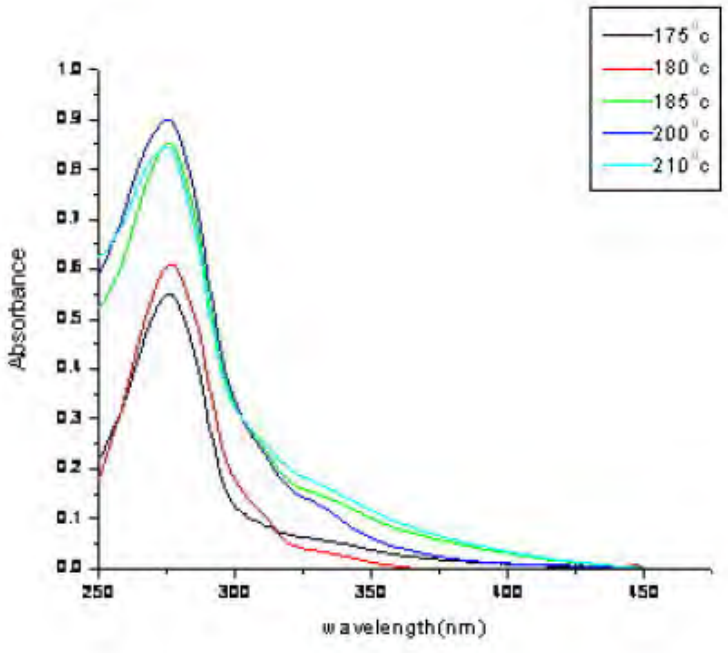

Fig. 4.10 Absorption spectra of caffeine at constant time $(6\,\mathrm{min})$ and several temperatures

The absorption spectra $(Fig.4.10)$ shows an increase and decrease in content of caffeine as function of roasting temperatures absorption maximum wavelength varies between 276.4 and $277.2\ nm$ Important parameters are summarized in table 4.8.

Table 4.8 different parameters of caffeine extracted from roasted and ground coffee at constant time $(6\,\mathrm{min})$ and several temperatures $(175 - 200^0 c)$.

degree of roast(^0c)	$\lambda_{\max}\ (nm)$	Absorbance	m$_i$ coffee(mg)	% of caffeine
green	275.6	0.3292	51.1	0.725
175	277.2	0.7227	50.9	1.22
180	276.4	0.6778	49.5	1.21
185	277.2	0.7331	51.0	1.43
190	276.4	0.6304	50.5	1.26
195	277.2	0.7178	51.9	1.33
200	276.2	0.6615	50.2	1.37

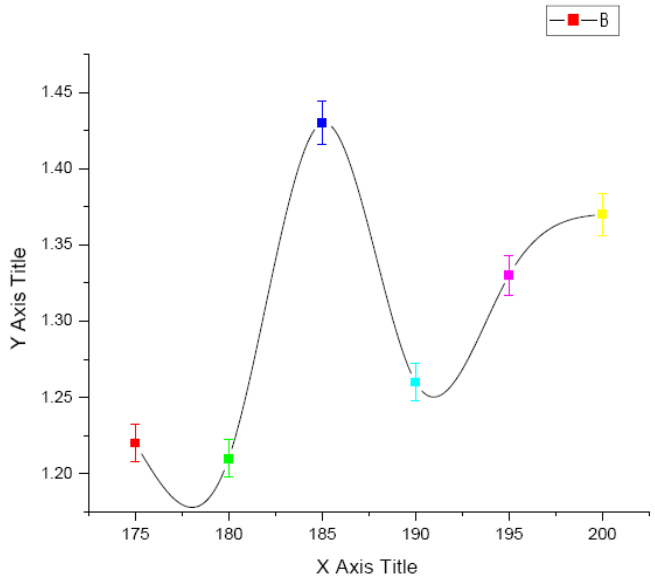

Fig. 4.11 Experimental influence of the degree of roast $\left(175 - 200^0 c\right)$ at $6\,\mathrm{min}$

The caffeine content $(Fig.4.11)$ shows an increase up to 185^0c heating. For roasting temperature greater than 185^0c a gradual decrease of caffeine content was observed.

For the sake of consistent,different parameters of caffeine extracted from roasted and ground coffee at constant time $(6\,\mathrm{min})$ and several temperatures are shown in the following tables.

Table 4.9 different parameters of caffeine extracted from roasted and ground coffee at constant time $(6\,\mathrm{min})$ and several temperatures $(172 - 205^0c)$.

degree of roast(^0c)	$\lambda_{\max}$	Absorbance	m$_i$ coffee(mg)	% of caffeine
green	275.6	0.3292	51.1	0.725
172	276.4	0.6873	51.2	1.261
181	277.2	0,5517	50.0	1.138
194	276.4	0.6411	50.3	1.303
198	276.4	0.9333	49.7	1.592
200	276.4	0.7348	49.5	1.34
205	274.8	0.5647	49.7	1.256

Table 4.10 different parameters of caffeine extracted from roasted and ground coffee at constant time $(6\,\mathrm{min})$ and several temperatures $(175 - 210^0c)$.

degree of roast(^0c)	$\lambda_{\max}\,(nm)$	Absorbance	m$_i$ coffee(mg)	% of caffeine
green	275.6	0.3292	51.1	0.725
175	275.6	0.5494	50.6	1.2
180	276.4	0.6317	51.5	1.085
185	275.6	0.8519	50	1.861
200	275.6	0.8988	50.4	1.774
210	274.0	0.8451	52	1.587

Using the same roasting protocol and experimental procedures to extract caffeine using dichlorometane for several temperatures $(172 - 205^0c)$ and constant roasting time $(6\,\mathrm{min})$ .The caffeine content varies as a function of roasting temperature.The absorption maximum wavelength observed $(Fig.4.12)$ varies between 274.8 and 277.2 nm.

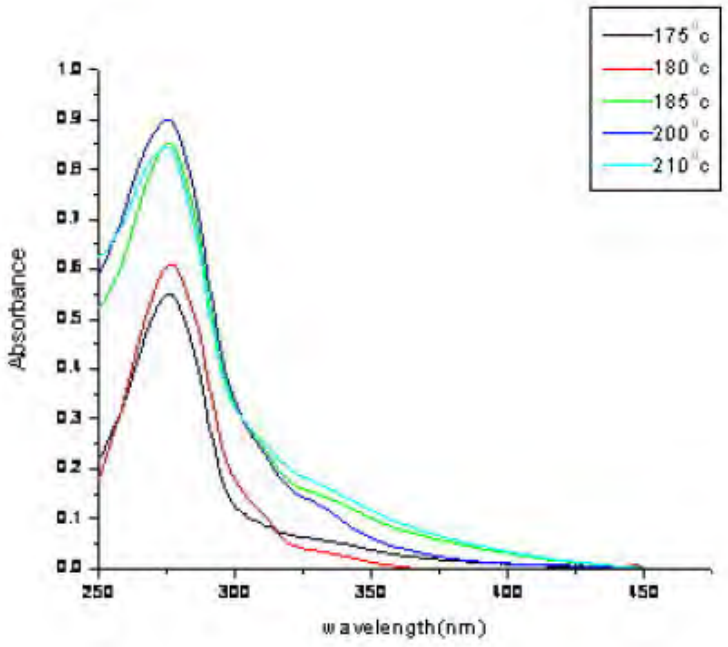

Fig. 4.12 Absorption spectra of caffeine at constant time $(6\,\mathrm{min})$ and several temperatures $(175 - 210^0 c)$

Using the same roasting protocol and experimental procedures to extract caffeine using dichlorometane for several temperatures $(175 - 210^0 c)$ and constant roasting time $(6\,\mathrm{min})$ .The caffeine content varies as a function of roasting temperature.The absorption maximum wavelength observed$(Fig\ 4.12)$ varies between 274 and 276.4nm.

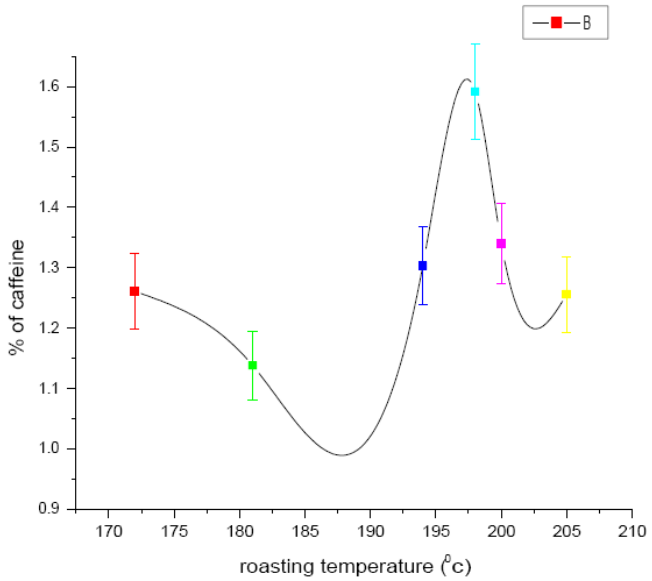

Fig. 4.13 Experimental influence of the roasting temprature $172 - 205^0 c$ at $6\,\mathrm{min}$

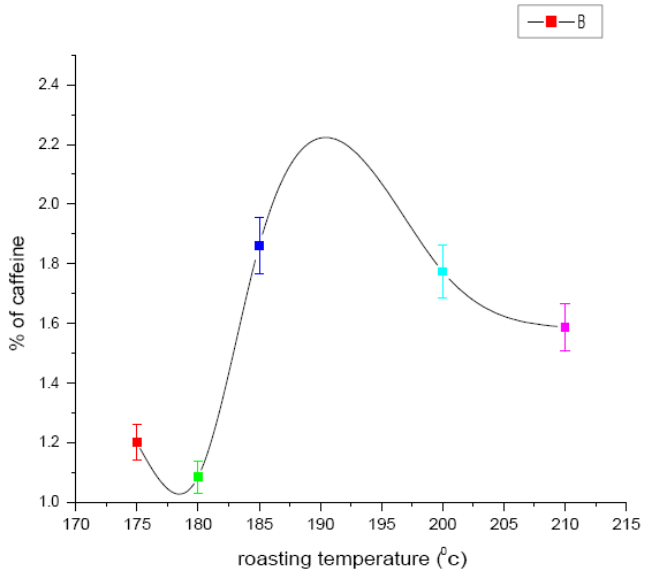

Fig. 4.14 Experimental influence of degree of roast $175 - 210^0 c$ at $6\,\mathrm{min}$

The caffeine content $(Fig.4.13)$ and $(Fig.4.14)$ shows similar trend as $(Fig.4.11)$. In $(Fig.4.13)$ there is an increase of caffeine content up to 198^0c degree of roast. For roasting temperature greater than 198^0c a gradual decrease of caffeine content was observed. Similarly $(Fig.4.14)$ shows an increase of caffeine content up to 185^0c degree of roast. For roasting temperature greater than 185^0c a gradual decrease of caffeine content was observed.

During the roasting of green coffee the bean temperature will be raised by a combination of external heating and exothermic chemical reactions, to above 200^0c. This temperature is well-inexcess to sublimation point of caffeine and thus it would to expected that considerable losses would be occur. However, it is found in practice that the losses are relatively modest. From $(Fig.4.11)$ the loss of caffeine occurs around 185^0c,$(Fig.4.13)$ the loss of caffeine occurs around 198^0c and $(Fig.4.14)$ the loss occurs around 185^0c, the losses observed are modest.The reason for this modest loss of caffeine are probably an increase in the sublimation point of caffeine as a result of pressure build up within the bean and a poor rate of diffusion of vapor through its outer layers. Caffeine also form salts as a result of the mildly acidic conditions which prevail within the bean, and which increase during roasting, but as these salts are relatively weak they will decompose and thus should have little effect on the sublimation process [19]. The graph of the average value of percentage of caffeine versus roasting temperature shows similar trend as [37] [38] .

The sources of error that may alter the exiperimental values are the following.

Random fluectuations, temperature effects, inhomogenous samples, spectrometric factors, wavelength accuracy, personal errors in measuring mass, an error during data analysis.

4.5 Thermal property of caffeine

In a thermogravimetric analysis the mass of a sample in a controlien atmosphere is recorded continuously as the temperature of the sample is increased (usually linearly with time) . A plot of mass or mas percent as a function of time is called a thermogram,or thermal decomposition curve.

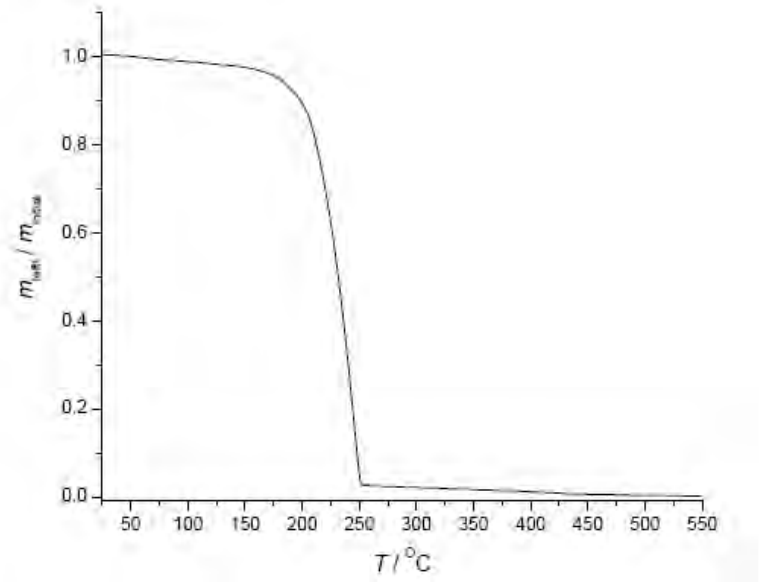

Fig. 4.15 TG curve for caffeine

The TG curve for caffeine is shown in $(\text{Fig}.4.15)$ indicates that it is stable at temperature up to 178^0c, when there begins the decomposition at 178^0c.The TG curve for pure caffeine shows one bending at 178^0c.

Chapter 5
Conclusion

In this study a simultaneous determination of caffeine was performed in a sample of coffee beans before and after roasting at either different temperature $140^0c - 210^0c$ or different exposure time $(4 - 10\,\mathrm{min})$. Caffeine from coffee was extracted by liquid-liquid extraction and interferences were removed by applying one Gaussian fit. A quantitative analysis of caffeine, in the coffee become feasible by uv/vis spectrophotometer system.

The objective of the study was investigation on the effects of roasting temperature and roasting time on caffeine content in coffee. For coffee roasted at constant temperature (170^0c) and variation of exposure time $(5 - 9\,\mathrm{min})$ the caffeine content increases up to $6\,\mathrm{min}$ of exposure time , and the loss of caffeine occurs around $6\,\mathrm{min}$. Similarly for 180^0c constant temperature and $(4 - 8\,\mathrm{min})$ exposure time the increase of caffeine extend to $7\,\mathrm{min}$ of exposure time and caffeine loss occurs around $7\,\mathrm{min}$. Finally for 200^0c constant temperature and $(4 - 8\,\mathrm{min})$ exposure time the loss of caffeine content occurs around $7\,\mathrm{min}$ of exposure time.The losses of caffeine observed are modest for the given constant temperature and variation of exposure time.

For coffee roasted at constant time $(6\,\mathrm{min})$ and several temperatures the average loss of caffeine occurs around 185^0c roasting temperaure. Similar to the roasting time a modest losses of caffeine were observed. By applying linear regression analy-

ses in the losses of coffee versus time data $(5 - 10\,\min)$ the rate constant for the thermochemical reactions in roasted coffee at 200^0c were calculated and its value is -0.0651.

As one can obsorve from the graph of percentage of caffeine versus temperature the caffeine content is relatively small around 180^0c degree of roast and more caffeine was obseerved around 185^0c. At a temperature greater than 185^0c there is a loss of caffeine but the sugars of the coffee are heavily caramelized and begins to be degraded, the aromatiic compounds, oils, and soluble solids are being burned out of the coffee.

Due to the physiological and psychological effect of caffeine, the roasting temperature 180^0c and a temperature greater than 185^0c are more advantageous becouse of small content of caffeine, but for the temperature greater than 185^0c the coffee losses its aromatic compounds, then it is more advantageous to use 180^0c as degree of roast.

Ethiopia exports coffee in its green form. Foreign companies like Starbucks uses Ethiopian name like Sidamo to market its coffee because consumers are willing to pay a premium price for these high quality coffees.The companies distributes the bulk of profits to roasters and retailers instead of producing countries.The efforts of these producing countries, farmers,traders,and exporters are directly damage the receiving of higher prices for their unique and high quality products.

By introducing different methods of caffeine extraction and roasting protocols to the exporting companies to export industrial processed coffee.Thus , further investigation is necessary to the time dependent of roasted and ground coffee and caffeine in coffee using optical methods.

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